

The University of Chicago

THE FREEZING POINTS OF  
CONCENTRATED AQUEOUS SODIUM  
CHLORIDE SOLUTIONS

A DISSERTATION SUBMITTED TO THE FACULTY  
OF THE DIVISION OF THE PHYSICAL SCIENCES  
IN CANDIDACY FOR THE DEGREE OF DOCTOR  
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY  
MARCH, 1934

By  
WALTER MATHIAS URBAIN

CHICAGO, ILLINOIS

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WALTER M. DE VRIES

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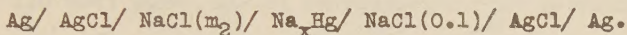
To Dr. T. F. Young, whose counsel and assistance in connection with this problem have proved invaluable, the author wishes to express his gratitude.



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## INTRODUCTION

Recently Harned and Nims<sup>1</sup> have made a detailed study of the thermodynamic properties of aqueous sodium chloride solutions by means of the cell:



Their measurements yield directly  $\mathcal{A}' / \mathcal{A}_0$ , the ratio of the activity coefficient  $\mathcal{A}'$  to the activity coefficient of the 0.1 molal sodium chloride solution. The value of this ratio, calculated from the activity coefficients tabulated by Lewis and Randall<sup>2</sup> for 4 molal (and 0.1 molal) sodium chloride solutions is about six per cent less than the value obtained from the measurements of Harned and Nims. The Lewis and Randall coefficients were derived from freezing point data and the relative partial molal heat content  $\bar{L}_1$ . In their calculations Lewis and Randall treated  $\bar{L}_1$  as a linear function of the temperature. Machin,<sup>3</sup> using the method of Young and Vogel<sup>4</sup> and Groenier,<sup>5</sup> determined the heat of dilution of sodium chloride solutions at various temperatures and showed that  $\bar{L}_1$  is not a linear function of the temperature. The

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<sup>1</sup>Harned and Nims, J. Am. Chem. Soc. 54, 423 (1932).

<sup>2</sup>Lewis and Randall, Thermodynamics (New York: McGraw-Hill Book Company, Inc., 1923).

<sup>3</sup>Machin, "The Variation of the Heats of Dilution of Sodium Chloride Solutions with Temperature" (Unpublished Doctor's thesis, University of Chicago, 1932).

<sup>4</sup>Young and Vogel, J. Am. Chem. Soc. 54, 3030 (1932), also Vogel, "The Relative Partial Molal Heat Contents of the Constituents of Aqueous Sodium Chloride Solutions" (Unpublished Doctor's thesis, University of Chicago, 1930).

<sup>5</sup>Groenier, "The Heats of Dilution of Sulphuric Acid Solutions" (Unpublished Doctor's thesis, University of Chicago, 1931).



introduction of these data into the calculation of the ratio  $\frac{T}{T_0}$  from freezing points yielded a value different from that obtained from electromotive force measurements by three per cent. The remaining discrepancy seemed to be due to the freezing points themselves.<sup>6</sup>

To find the exact source and to remove as much as possible of this discrepancy the freezing points of aqueous solutions of sodium chloride were investigated in the range from 0.1 to about 4.65 molal, and from these data new values of the ratio  $\frac{T}{T_0}$  were calculated.

#### THE APPARATUS

The apparatus was the same as that used by Harkins and Wampler<sup>7</sup> except for the following modifications:

The contents of the Dewar bulb, A, Figure 1, which contained ice and water to serve as a reference temperature for the thermels, were stirred by a paddle-wheel stirrer, B. To permit sturdier construction, this stirrer and its protector tube, C, were made of monel metal instead of glass. The stirrer shaft and the support for the protector tube were both broken by a small section of bakelite, D, at the brass plate, E-E, supporting them to cut down heat leakages into the Dewar bulb. The speed with which this stirrer revolved was found to be unimportant; it usually operated at about six hundred revolutions per minute.

The contents of the other Dewar, N, were stirred by means of a hand stirrer, M, manipulated through a small brass tube, I. This stirrer consisted of a ring of nickel secured to a rod of the same material. This in turn was fastened to a wooden handle in

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<sup>6</sup>Young, Chem. Rev. 13, 103 (1933).

<sup>7</sup>Harkins and Wampler, J. Am. Chem. Soc. 53, 850 (1931).



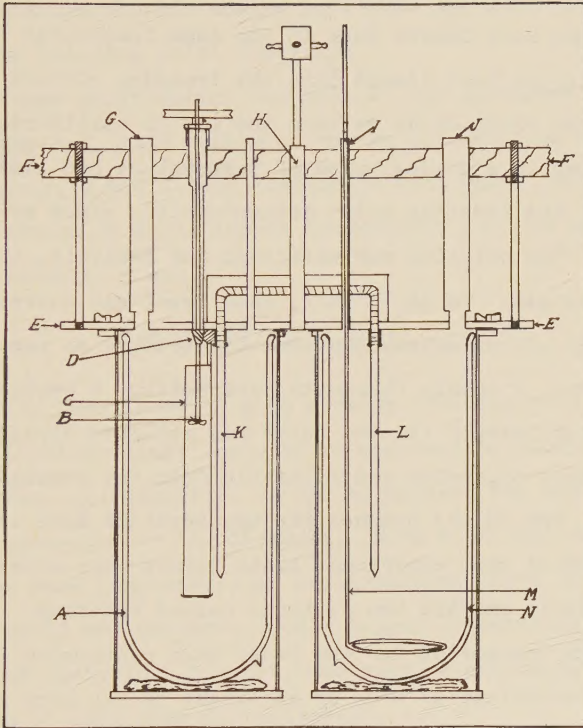


Figure 1.

such a manner that only the nickel came into contact with the solution. A paddle-wheel stirrer, like that in the other Dewar, was found to give insufficient stirring of the freezing mixture. The ring stirrer, moving through the whole depth of the Dewar, proved to be quite effective.

When both Dewars were in the same thermostat bath at  $0^{\circ}\text{C}.$ , sufficient heat leaked into the freezing mixture Dewar, N, to dilute the solution by melting the ice in equilibrium with it. This resulted in a gradual rise of temperature and limited the accuracy of the freezing point determination, since by the time a sample of the solution was withdrawn for analysis, the temperature had changed. To avoid this, each Dewar was surrounded by a bath kept at approximately the same temperature as the contents of the Dewar. A double thermostat was built. A section, H, of the partition between the two baths was attached directly to the freezing point apparatus and separable from the remainder of the partition. The joints between the two sections were carefully milled. Before each experiment these joints were covered with petroleum jelly and the two sections bolted together.

The thermostat for the Dewar bulb containing ice and water was maintained at  $0^{\circ}\text{C}.$  by an excess of ice kept in a bath of water. It was stirred vigorously by a stirrer protected from the ice by means of a screen over its intake.

The other thermostat was identical except that ice and a rock-salt brine were used to secure the temperatures below  $0^{\circ}\text{C}.$  It was usually operated at a temperature a half degree to a degree warmer than that of the freezing mixture within the Dewar.

The baths of the thermostats reached up to the oak board, F-F, on the top of the apparatus (about ten centimeters above the Dewars). The thermostating permitted very little heat to leak

into the Dewars. As a result, no difficulty was encountered in obtaining nearly constant temperatures inside the Dewars during the freezing point determinations. During the maximum period required (two minutes) for the temperature measurement and the removal of a sample of the solution for analysis, the temperature of the freezing mixture did not change more than one-hundredth of a per cent of the freezing point lowering.

One other modification was made in the apparatus of Harkins and Wampler. This consisted in the introduction of two large brass tubes, G and J, one leading to each Dewar, which allowed the insertion of a resistance thermometer for the calibration of the thermels, K and L.

#### THE ELECTRICAL CIRCUIT

A White potentiometer with a range from 0.0 to 0.1 volt in steps of ten microvolts, employed in conjunction with a type HS low resistance galvanometer, served to measure the electromotive force generated by the thermels. With both legs of the thermel at the same temperature an electromotive force of not more than 0.1 microvolt was observed. Only copper connections were employed in the electrical circuit, and stray electromotive forces never amounted to more than 0.3 microvolt.

#### CALIBRATION OF THE THERMELS

A platinum resistance thermometer, used in conjunction with a Mueller Wheatsone bridge, was employed in the calibration of the thermels. The bridge was kept in an air thermostat maintained within  $.05^{\circ}$  of  $23^{\circ}\text{C}$ . To obtain this temperature in warm weather, compressed air, previously blown through a vertical five-foot stove-pipe filled with ice and water, was passed into



the thermostat. When this gave insufficient cooling, a pail of ice was put directly into the thermostat. About twelve hours before the bridge was to be used, the thermostat was started to allow time for the coils to come to temperature equilibrium. Both the resistance thermometer and the Mueller bridge were calibrated by the United States Bureau of Standards, the latter at 23°C.

Since bridge measurements could be obtained with a precision of .0001 ohm, it was essential that all contacts be clean. The coil taps were frequently washed with alcohol, and before each measurement the switch levers were run over them several times to scrape a fresh surface.

It was found necessary to check the balance of the two arms of the bridge before every measurement. Sometimes the balance would be maintained for days and at other times readjustment was needed an hour after a previous setting. This balancing necessitated the removal of certain wires, and considerable care was required to secure connections of low (or constant) resistance when the wires were replaced.

For the calibration of the thermels the resistance thermometer was inserted through the brass tubes, G and J, Figure 1. Constant temperatures for the calibration were obtained by means of equilibrium mixtures of ice and calcium chloride solutions of the proper strength to give the desired temperature. The following empirical equation was derived to express the temperature,  $t$ , in terms of the electromotive force,  $E$ , in microvolts:

$$t = 1.0480(10^{-3}E) - 1.042(10^{-9}E^2) + 1.17(10^{-14}E^3)$$

In Figure 2 is shown the deviation of the observed temperature from this equation. The maximum disagreement is not greater than .15 per cent; the mean is about .05 per cent. This

equation was checked frequently during the course of the experiments; no noticeable change could be observed although the thermel was taken apart several times for drying after water had entered it.

In the calibration of the thermel one anomalous phenomenon was observed. When each thermostat was operated at the temperature of the contents of its respective Dewar, the resistance thermometer gave erratic results when placed in the Dewar below  $0^{\circ}\text{C}.$ , but was perfectly consistent in the  $0^{\circ}$  Dewar. When the thermostat around the sub-zero Dewar was operated at  $0^{\circ}$ , consistent temperatures were recorded. No explanation could be found for this phenomenon. The head of the thermometer, due to its position, was at the temperature of the surrounding thermostat. As far as could be observed, the effect was not due to moisture collecting on the head of the thermometer. Possibly the effect was due to a varying temperature gradient down the thermometer, but an experiment showed this to be very small.

The difficulty was avoided by calibration of the thermels when the whole apparatus was surrounded by a bath at  $0^{\circ}\text{C}.$  However, this procedure limited, to a certain extent, the precision of the calibration, particularly in the more concentrated solutions where the temperature changed rapidly due to heat leakages. The adiabatic thermostating of each Dewar during the calibration would have been desirable, for it would have permitted the calibration of the thermels under the same conditions they were to be used, and in addition would have increased the precision of the calibration by the prevention of temperature changes during the measurements.

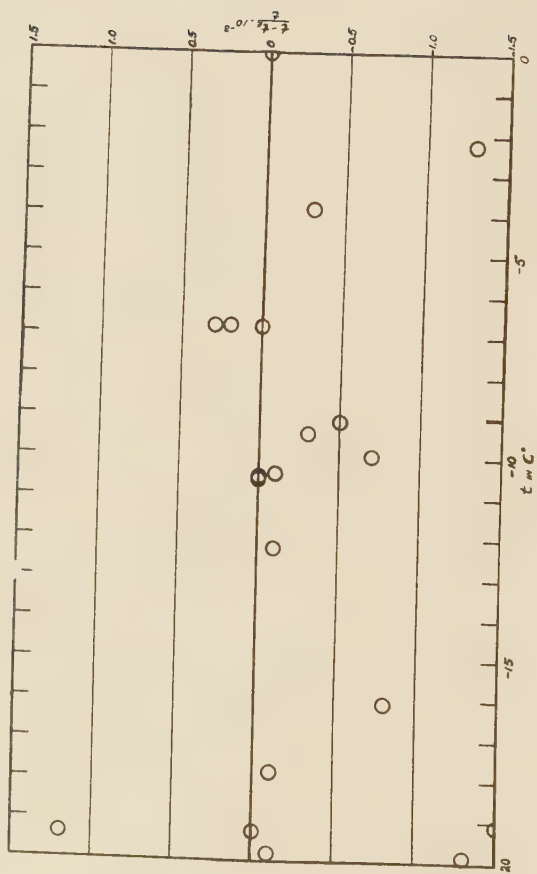


Figure 2.



## MATERIALS

Baker's analyzed fused sodium chloride was used throughout the experiment. Boiled distilled water was used for the solutions and in the reference Dewar. Clear commercial ice was employed entirely.

## EXPERIMENTAL PROCEDURE

The ice was first crushed in a mechanical crusher, which produced pieces about two by five centimeters. These were then pressed through an iron grating, yielding pieces about one centimeter in diameter. This cracked ice was then washed first with tap water, then with distilled and finally with the water used to make up the solutions.

About four hundred grams of this ice was placed in the reference Dewar and enough boiled distilled water, cooled to  $0^{\circ}\text{C}.$ , was added to make the level of the mixture come to about two centimeters from the brass plate, E-E, Figure 1.

The freezing mixture was prepared from a solution of somewhat greater strength than was desired. It was cooled until it began to freeze. It was then added to some of the prepared ice in a beaker and the mixture vigorously stirred. A sufficient amount of this mixture was put into the other Dewar to make the level the same as in the reference Dewar. The apparatus was then assembled and placed in the thermostat baths. The temperature of the bath around the freezing mixture Dewar was adjusted to within a degree of the temperature of its contents. The motor driven stirrer in the reference Dewar was started.

The freezing mixture was stirred and a series of temperature readings were made. This was continued until a steady state

was reached, as was evidenced by no change of temperature or at most a slow steady drift after repeated stirring. The mixture was not stirred during an actual temperature measurement. Five to thirty minutes were required for the establishment of this steady state; dilute solutions required a shorter time than the more concentrated ones. When the steady state had been reached, and the temperature observed, approximately one hundred cubic centimeters of the solution were withdrawn in a pipette inserted through tube J, Figure 1. This solution was replaced by an equal quantity of water, cooled to  $0^{\circ}\text{C}.$ , so that the freezing point of a solution of another concentration could be determined. The approximate temperature at which this more dilute solution came into equilibrium with the ice was observed and the thermostat adjusted to a slightly higher temperature. A new freezing point was determined as outlined above. It was usually possible to obtain at least four freezing points from one charge of ice.

#### ANALYSIS OF SOLUTIONS

Two methods of analysis were used. Some solutions more concentrated than one molal were analyzed by the sodium chloride residue method of Richards and Hall.<sup>8</sup> Weighed quantities of the solutions were evaporated in loosely stoppered Erlenmeyer flasks at  $150^{\circ}$  to  $175^{\circ}\text{C}.$  The salt was then heated in the flasks at  $350^{\circ}$  to  $400^{\circ}$  for twelve hours and weighed. As this proved to be a rather slow process, and since it was advisable to check the results by a second method, the remainder of the solutions were analyzed by electrical conductivity. Solutions more concentrated than one molal were diluted by weight until a solution which fell

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<sup>8</sup>Richards and Hall, J. Am. Chem. Soc. 51, 709 (1929).

into the range 0.1 to 1.0 molal was obtained. Solutions whose molality fell within that range were analyzed directly without dilution. A diagram of the conductivity cell used in the analyses is shown in Figure 3. A 0.1 molal solution had a resistance of about 14,000 ohms in this cell and a 1 molal of about 1800.

The resistance of each of twenty-two solutions was measured in the cell. These solutions were made up to an accurately known molality. It was found that  $1/mr$  ( $m$  is molality,  $r$  is the resistance of the solution in the cell) could be represented approximately by the following equation:

$$1/mr = -0.009,561,414(1/\sqrt{r}) + 0.000,769,460,6 \quad (1)$$

The exact relationship is given by equation (2):

$$1/mr = -0.009,561,414(1/\sqrt{r}) + 0.000,769,460,6 + \epsilon \quad (2)$$

The values of  $\epsilon$ , determined from the calibration, were plotted on a very large scale as a function of  $1/\sqrt{r}$ . This is shown in Figure 4. To obtain the molal concentration of the solution whose resistance in the cell was known, the value of  $\epsilon$  is determined from the plot, and  $1/mr$  is evaluated from equation (2). From this  $m$  is obtained directly.

This type of calibration cancelled all constant errors in the method, and the analyses were very rapid. The cell during a measurement was kept in an oil thermostat at  $25.00^\circ\text{C.} \pm .02^\circ$ .

A Wheatstone bridge, using a microphone hummer as a source of 1000 cycle alternating current and employing a two stage audio frequency amplifier, was used for the measurement of resistance. All electrical connections were made with lead-sheathed solid wire and the sheath grounded. The apparatus was placed on grounded tin plates. However, such shielding was found to be unnecessary, and according to Jones and Josephs<sup>9</sup> inadvisable. A

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<sup>9</sup>Jones and Josephs, J. Am. Chem. Soc. 50, 1049 (1928).

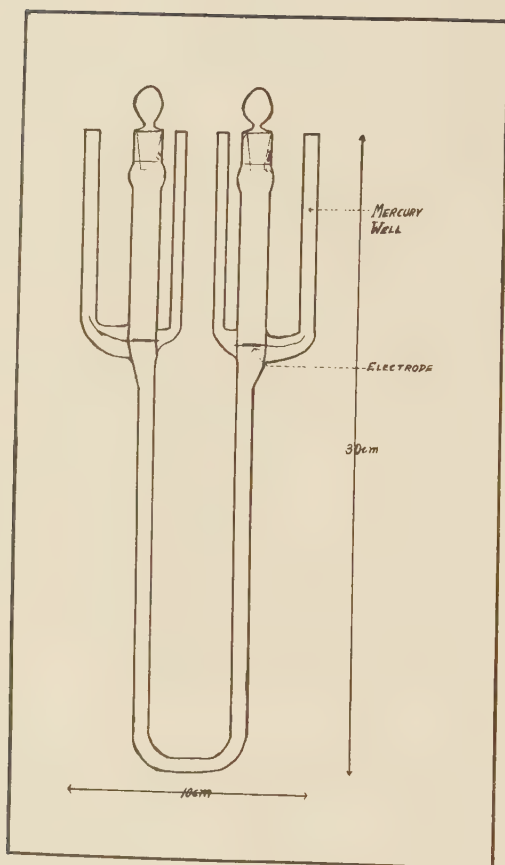


Figure 3.



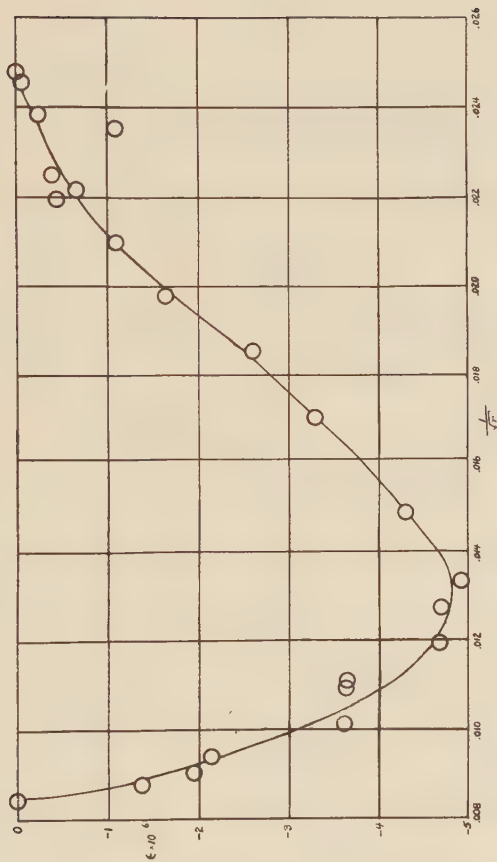


Figure 4.

diagram of the connections and set-up is shown in Figure 5.

The two methods of analysis yielded very closely the same results. Table I shows the results of an analysis of a "standard" solution by the two methods.

TABLE I

|                                          |        | <u>% Error</u> |
|------------------------------------------|--------|----------------|
| Molality as made up                      | 2.7134 | (0.00)         |
| Molality by gravimetric (residue) method | 2.7159 | 0.092          |
| Molality by conductivity                 | 2.7149 | 0.055          |

All weights were corrected to weight in vacuo.

# RESULTS

Table II shows the values of the freezing point lowerings,  $\Delta$ , of solutions of molality,  $m$ .

## CALCULATION OF THE RATIO $\gamma/\gamma_{0.1}$ AND DISCUSSION OF THE RESULTS

The thermodynamic considerations and the accuracy of the calculation of the activity coefficient of a solute from the freezing points of its solutions have been discussed in detail by Young.<sup>10</sup> For our purposes the activity coefficient ratio is obtained with sufficient accuracy from the following expression:

$$\log \gamma/\gamma_{0.1} = - \int_{0.1}^m j d \log m - \frac{j-j_{0.1}}{2.3026} + \frac{B_2}{\nu} \int_{0.1}^m \frac{\nu}{m} d\nu \\ + \frac{C_2}{2\nu} \int_{0.1}^m \frac{\nu}{m} d(\nu^2) - \frac{55.508}{\nu} \int_{0.1}^m \frac{dx}{m}$$

where the various quantities have the meaning assigned by Young.

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<sup>10</sup>Young, Chem. Rev. loc cit.



TABLE II

| Urbain             |                    |                    | Scatchard |        |
|--------------------|--------------------|--------------------|-----------|--------|
| m                  | $\mathcal{J}$      | j                  | m         | j      |
| .1010 <sub>1</sub> | .3524              | .0615 <sub>7</sub> | .000819   | -.0092 |
| .1074 <sub>4</sub> | .3729              | .0663 <sub>5</sub> | .005120   | .0192  |
| .1380 <sub>7</sub> | .4776              | .0695 <sub>5</sub> | .013540   | .0338  |
| .1462 <sub>2</sub> | .505 <sub>4</sub>  | .0702 <sub>7</sub> | .033489   | .0472  |
| .1878 <sub>3</sub> | .646 <sub>5</sub>  | .0741 <sub>8</sub> | .078838   | .0632  |
| .1985 <sub>8</sub> | .683 <sub>3</sub>  | .0743 <sub>8</sub> | .12579    | .0714  |
| .2184 <sub>8</sub> | .749 <sub>3</sub>  | .0774 <sub>4</sub> | .22318    | .0807  |
| .2851 <sub>6</sub> | .975 <sub>8</sub>  | .0795 <sub>2</sub> | .001866   | .0096  |
| .3767 <sub>1</sub> | 1.281 <sub>2</sub> | .0851 <sub>8</sub> | .008605   | .0269  |
| .4235 <sub>7</sub> | 1.436 <sub>8</sub> | .0875 <sub>7</sub> | .022648   | .0449  |
| .4850 <sub>3</sub> | 1.645 <sub>9</sub> | .0871 <sub>8</sub> | .054924   | .0557  |
| .5226 <sub>8</sub> | 1.771 <sub>3</sub> | .0884 <sub>2</sub> | .10371    | .0672  |
| .713 <sub>8</sub>  | 2.41 <sub>3</sub>  | .0908 <sub>2</sub> | .15765    | .0747  |
| .723 <sub>8</sub>  | 2.44 <sub>4</sub>  | .0916 <sub>6</sub> | .41547    | .0885  |
| .741 <sub>1</sub>  | 2.50 <sub>8</sub>  | .0910 <sub>2</sub> | .35492    | .0867  |
| .812 <sub>2</sub>  | 2.75 <sub>0</sub>  | .0893 <sub>2</sub> | .43370    | .0888  |
| .877 <sub>1</sub>  | 2.96 <sub>7</sub>  | .0900 <sub>6</sub> | .53070    | .0903  |
| .968 <sub>3</sub>  | 3.27 <sub>8</sub>  | .0893 <sub>7</sub> | .64857    | .0912  |
| 1.032 <sub>1</sub> | 3.49 <sub>5</sub>  | .0891 <sub>3</sub> | .80120    | .0911  |
| 1.155 <sub>4</sub> | 3.92 <sub>9</sub>  | .0852 <sub>8</sub> | .99853    | .0888  |
| 1.204 <sub>7</sub> | 4.09 <sub>5</sub>  | .0857 <sub>2</sub> | 1.2774    | .0849  |
| 1.317 <sub>7</sub> | 4.49 <sub>2</sub>  | .0831 <sub>0</sub> | .18703    | .0779  |
| 1.437 <sub>1</sub> | 4.92 <sub>1</sub>  | .0788 <sub>4</sub> | .27394    | .0835  |
| 1.608 <sub>1</sub> | 5.53 <sub>1</sub>  | .0748 <sub>2</sub> | .48597    | .0896  |
| 1.662 <sub>2</sub> | 5.72 <sub>1</sub>  | .0741 <sub>2</sub> | .59159    | .0906  |



TABLE II (Cont.)

| Urbain             |                    |                     | Scatchard |       |
|--------------------|--------------------|---------------------|-----------|-------|
| m                  | $\lambda$          | j                   | m         | j     |
| 1.846 <sub>2</sub> | 6.39 <sub>3</sub>  | .0684 <sub>9</sub>  | .72518    | .0911 |
| 2.267 <sub>1</sub> | 7.97 <sub>7</sub>  | .0535 <sub>2</sub>  | .90133    | .0898 |
| 2.329 <sub>1</sub> | 8.21 <sub>9</sub>  | .0508 <sub>3</sub>  | 1.1540    | .0866 |
| 2.351 <sub>9</sub> | 8.31 <sub>5</sub>  | .0490 <sub>2</sub>  |           |       |
| 2.559 <sub>6</sub> | 9.12 <sub>2</sub>  | .0413 <sub>6</sub>  |           |       |
| 2.747 <sub>0</sub> | 9.88 <sub>3</sub>  | .0322 <sub>8</sub>  |           |       |
| 3.003 <sub>1</sub> | 10.93 <sub>7</sub> | .0203 <sub>6</sub>  |           |       |
| 3.069 <sub>1</sub> | 11.20 <sub>7</sub> | .0177 <sub>6</sub>  |           |       |
| 3.351 <sub>4</sub> | 12.42 <sub>0</sub> | .00315              |           |       |
| 3.457 <sub>8</sub> | 12.88 <sub>3</sub> | -.00218             |           |       |
| 3.568 <sub>4</sub> | 13.37 <sub>2</sub> | -.00801             |           |       |
| 3.811 <sub>8</sub> | 14.49              | -.0222 <sub>7</sub> |           |       |
| 3.884 <sub>2</sub> | 14.81              | -.0259 <sub>6</sub> |           |       |
| 4.242 <sub>8</sub> | 16.53              | -.0482 <sub>0</sub> |           |       |
| 4.445 <sub>0</sub> | 17.52              | -.0603 <sub>9</sub> |           |       |
| 4.454 <sub>6</sub> | 17.55              | -.0597 <sub>0</sub> |           |       |
| 4.523 <sub>5</sub> | 17.92              | -.0658 <sub>5</sub> |           |       |
| 4.655 <sub>7</sub> | 18.59              | -.0741 <sub>7</sub> |           |       |
| 4.677 <sub>8</sub> | 18.67              | -.0736 <sub>6</sub> |           |       |

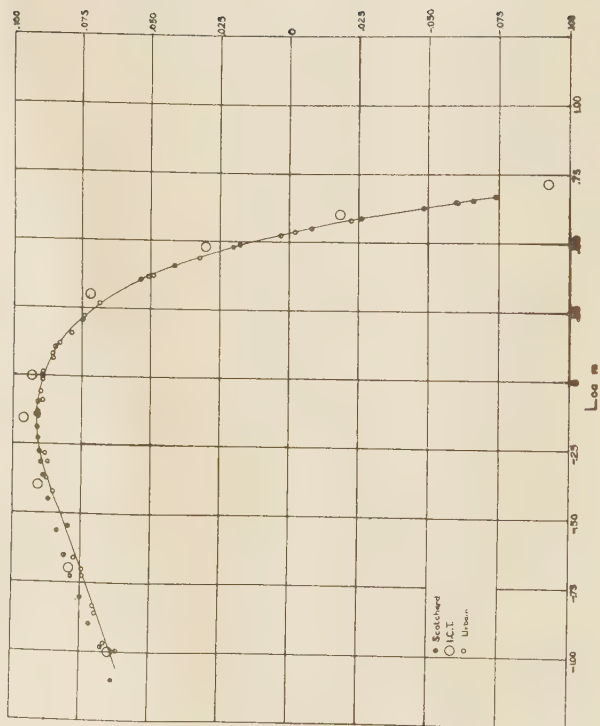


Figure 6.

For convenience Appendix I defines all terms.

Table IV lists the various steps in the calculation of the ratio  $\gamma/\gamma_{0.1}$ .

The evaluation of the integral

$$- 55.508 \int_{0.1}^m \frac{dx}{m}$$

was obtained as follows:

$$\int_{0.1}^{m=m'} \frac{1}{m} \cdot dx = \left( \frac{x}{m'} - \frac{x}{m_{0.1}} \right) - \int_{0.1}^{m'} \frac{x}{m^2} dm$$

Figure 7 shows  $x/m^2$  plotted against  $m$ . The area under this curve up to a given concentration yields the value of the integral

$$\int_{0.1}^{m'} \frac{x}{m^2} dm$$

This, added to the proper value of  $x/m' = x/m_{0.1}$ , is the value of the integral

$$\int_{0.1}^m \frac{dx}{m}$$

The magnitude of this integral in the region from 0.1 to 0.2 molal was also determined by mechanical integration of the curve obtained by plotting  $1/m$  versus  $x$ . This second method of integration yielded a result which agreed within 0.2 per cent of that of the first. An error of this magnitude in the value of the above integral would affect the value of the ratio  $\gamma/\gamma_{0.1}$  by less than 0.001 per cent.

The freezing points of sodium chloride solutions up to about 1 molal have recently been investigated by Scatchard.<sup>11</sup> Table II includes his data. The results of a calculation of  $\gamma/\gamma_{0.1}$  from his data and from the data of this investigation from 1.0 to 4.5 molal are incorporated into Table V.

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<sup>11</sup>Scatchard, Private communication.

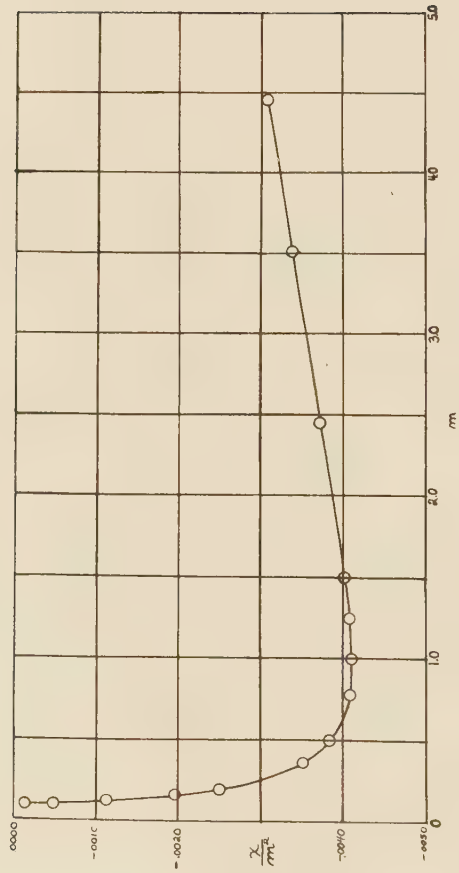


Figure 7.

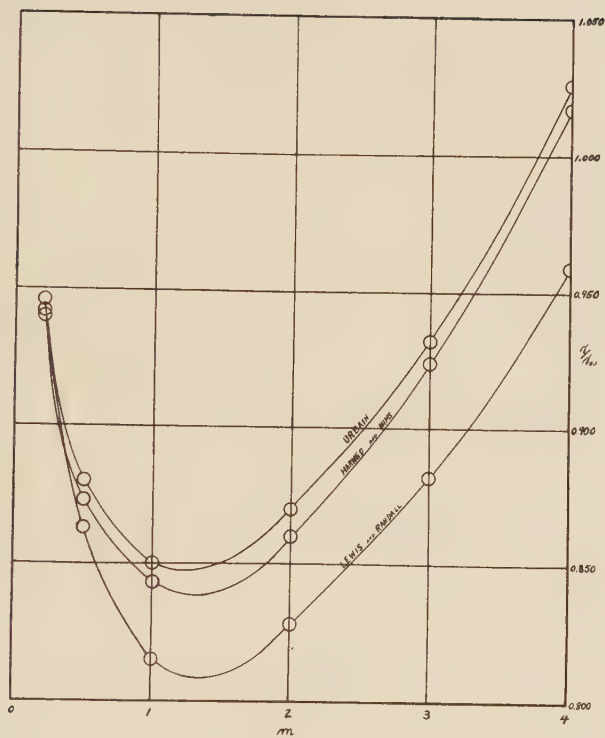


Figure 8.



TABLE III

Evaluation of  $\mathbf{x}$ 

| $m$                | $\sqrt{m}$          | $\psi$             | $\bar{L}_1''$<br>25° | $\bar{C}_P - \bar{C}_P^0$<br>0° | $\frac{C}{\Delta T}$<br>$\frac{\Delta T}{\Delta}$ | $b + 50c$<br>$(\bar{C}_P - \bar{C}_P^0)''$ | $\frac{2c}{d^2 \bar{L}_1}$<br>$\frac{d^2 \bar{L}_1}{d^2 z}$ | $\bar{L}_1'' + \Delta \bar{C}_P z - \Delta T \Omega$<br>$\mathbf{x}$ |
|--------------------|---------------------|--------------------|----------------------|---------------------------------|---------------------------------------------------|--------------------------------------------|-------------------------------------------------------------|----------------------------------------------------------------------|
| 4.458 <sub>1</sub> | 2.1114 <sub>3</sub> | 17.58 <sub>7</sub> | 21.16                | -1.4756                         | .008928                                           | -1.0292                                    | .01785 <sub>6</sub>                                         | -.006108 <sub>9</sub>                                                |
| 3.513 <sub>5</sub> | 1.8744 <sub>4</sub> | 13.13 <sub>5</sub> | 19.73                | -1.1672                         | .008640                                           | -.7352                                     | .01728                                                      | -.004177 <sub>5</sub>                                                |
| 2.450 <sub>4</sub> | 1.5653 <sub>9</sub> | 8.69 <sub>1</sub>  | 13.44                | -.8056                          | .007680                                           | -.4216                                     | .01536                                                      | -.002231 <sub>7</sub>                                                |
| 1.502 <sub>3</sub> | 1.2256 <sub>9</sub> | 5.149 <sub>4</sub> | 6.306                | -.4272                          | .004307 <sub>2</sub>                              | -.21184                                    | .008614 <sub>4</sub>                                        | -.000906 <sub>0</sub>                                                |
| 1.250 <sub>0</sub> | 1.1180 <sub>3</sub> | 4.252 <sub>1</sub> | 4.576                | -.3318 <sub>4</sub>             | .003545 <sub>6</sub>                              | -.15456                                    | .007091 <sub>2</sub>                                        | -.000636 <sub>1</sub>                                                |
| 1.000 <sub>0</sub> | 1.00000             | 3.387 <sub>5</sub> | 2.982                | -.2417 <sub>6</sub>             | .002881 <sub>6</sub>                              | -.10768                                    | .005363 <sub>2</sub>                                        | -.000410 <sub>2</sub>                                                |
| .7772 <sub>0</sub> | .88159              | 2.626 <sub>4</sub> | 1.765                | -.16628                         | .001891 <sub>2</sub>                              | -.07172                                    | .003782 <sub>4</sub>                                        | -.000246 <sub>6</sub>                                                |
| .4973 <sub>6</sub> | .70524              | 1.685 <sub>5</sub> | .628                 | -.07896                         | .000908 <sub>8</sub>                              | -.03352                                    | .0018176                                                    | -.000094 <sub>8</sub>                                                |
| .3600 <sub>0</sub> | .60000              | 1.225 <sub>6</sub> | .2598                | -.045408                        | .000526 <sub>08</sub>                             | -.019104                                   | .0010521 <sub>6</sub>                                       | -.000045 <sub>6</sub>                                                |
| .1951 <sub>4</sub> | .44175              | .6711              | .0145                | -.015768                        | .000200 <sub>32</sub>                             | -.005752                                   | .0004006 <sub>4</sub>                                       | -.000009 <sub>5</sub>                                                |
| .1600 <sub>0</sub> | .40000              | .5520              | -.0098               | -.011596                        | .000162 <sub>24</sub>                             | -.003484                                   | .0003244 <sub>8</sub>                                       | -.000005 <sub>02</sub>                                               |
| .1225 <sub>0</sub> | .35000              | .4247              | -.0232               | -.007376                        | .000112 <sub>64</sub>                             | -.001744                                   | .0002252 <sub>8</sub>                                       | -.000001 <sub>70</sub>                                               |
| .1000 <sub>0</sub> | .31623              | .3481              | -.0259               | -.005072                        | .000079 <sub>36</sub>                             | -.001104                                   | .00015872                                                   | -.000000 <sub>43</sub>                                               |
| .0954 <sub>6</sub> | .30897              | .3326              | -.0327               | -.004664                        | .000061 <sub>44</sub>                             | -.001592                                   | .00012288                                                   | -.000000 <sub>12</sub>                                               |

TABLE IV  
Calculation of  $\eta/\eta_0$

| $m$ | $\int_{0.1}^m \eta d \log m$ | $-\frac{\eta_m - \eta_{0.1}}{2.3026}$ | $0.11947 \int_{0.1}^m \frac{\eta d\eta}{\eta}$ | $-0.14958 \int_{0.1}^m \frac{\eta d(\eta')}{\eta}$ | $\log \eta' \eta'_{0.1-m}$ | $\eta' \eta'_{0.1-m}$ | $\frac{55508}{2} \int_{0.1}^m \frac{dx}{\eta}$ | $\eta/\eta_{0.1-m}$ |
|-----|------------------------------|---------------------------------------|------------------------------------------------|----------------------------------------------------|----------------------------|-----------------------|------------------------------------------------|---------------------|
| .1  | -.000000                     | -.000000                              | .000000                                        | .000000                                            | .000000                    | 1.00000               | 1.00000                                        | (1.00000)           |
| .2  | -.020999                     | -.005081                              | .000140                                        | -.000002                                           | .974058-1                  | .94202                | 1.00413                                        | .945 <sub>9</sub>   |
| .5  | -.053724                     | -.010814                              | .000550                                        | -.000014                                           | .935998-1                  | .86297                | 1.01969                                        | .880 <sub>0</sub>   |
| 1.0 | -.080950                     | -.010901                              | .001234                                        | -.000058                                           | .909325-1                  | .81157                | 1.04745                                        | .850 <sub>1</sub>   |
| 2.0 | -.104660                     | .000217                               | .002699                                        | -.000248                                           | .898008-1                  | .79069                | 1.09979                                        | .869 <sub>6</sub>   |
| 3.0 | -.112533                     | .018631                               | .004381                                        | -.000625                                           | .909854-1                  | .81256                | 1.14719                                        | .932 <sub>2</sub>   |
| 4.0 | -.112036                     | .042517                               | .006374                                        | -.001282                                           | .935573-1                  | .86213                | 1.18957                                        | 1.025 <sub>6</sub>  |
| 4.5 | -.107742                     | .055242                               | .007498                                        | -.001749                                           | .953249-1                  | .89794                | 1.20758                                        | 1.084 <sub>3</sub>  |

TABLE V

| m        | L. and R. | I. C. T. | U.    | S. and U. | H. and N. |
|----------|-----------|----------|-------|-----------|-----------|
| 0.2      | .942      | .942     | .946  | .944      | .940      |
| 0.5      | .863      | .871     | .880  | .878      | .873      |
| 1.0      | .815      | .839     | .850  | .849      | .843      |
| 2.0      | .828      | .851     | .870  | .869      | .860      |
| 3.0      | .882      | .908     | .932  | .931      | .924      |
| 4.0      | .959      | .988     | 1.026 | 1.024     | 1.017     |
| 4.5      | ----      | ----     | 1.084 | 1.083     | -----     |
| Per Cent | 5.7       | 2.9      | 0.86  | 0.77      | (0.00)    |

Table V shows a comparison of the values of the ratio,  $\gamma/\gamma_{0.1}$ , from various sources: Lewis and Randall,<sup>12</sup> International Critical Tables as calculated by Young,<sup>13</sup> Urbain, Scatchard and Urbain, and Harned and Nims<sup>14</sup> from electromotive force measurements. For comparison the last line of the table indicates the per cent deviation at four molal from the results of Harned and Nims. In Figure 8 the activity coefficient, as obtained from some of the sources mentioned above, is shown plotted against the molality.

The discrepancy has been reduced to less than one per cent at four molal and is now of the opposite sign to that existing before. The difference between Scatchard's data and those of this investigation is so small that the corresponding activity

<sup>12</sup>Lewis and Randall, loc. cit.

<sup>13</sup>Young, Chem. Rev. loc. cit.

<sup>14</sup>Harned and Nims, loc. cit.

coefficients are essentially the same. The very small remaining discrepancy between the electromotive force measurements and the freezing point determinations is probably not primarily due to errors in the cryoscopic measurements. Other factors can easily account for the difference.

Harned and Nims referred all their data to the 0.1 molal solution in one half of their cell. If a side reaction occurred in this solution, as was quite possible, all their data would be in error. An error in this particular solution might have a greater effect on all the results than the estimated individual errors in each of the more concentrated solutions. If this were the case, all the values of the ratio,  $\gamma/\gamma_0$ , obtained from electromotive force data would differ by nearly a constant amount from those of the freezing points. An examination of the results shows that the percentage difference between the two sets of activity coefficient ratios is almost constant from 1.0 to 4.0 molal.

The nature of the calculation of the activity coefficient from freezing points consists in first the calculation of the rate of change of the activity of the solvent with concentration. Then by means of the equation

$$d \ln a_2 = - \frac{N_1}{N_2} d \ln a_1$$

the rate of change of the activity of the solute is obtained from that of the solvent. The ratio  $N_1/N_2$  is very large below one molal, and any error in the rate of change of the activity of the solvent is made more prominent. While the source of these errors may still lie in the freezing points, other factors can account for the errors. The heat of dilution data may not yet be complete enough to yield the true temperature coefficient of

$\bar{L}_1$ . It is noteworthy that the heat capacities of sodium chloride solutions at 25°C. calculated from the heats of dilution data differ from the values obtained by direct measurements by Randall and Rossini.<sup>15</sup>

In addition to these errors there exist the errors in  $\Delta H_\Theta$  and R mentioned by Young.<sup>16</sup>

A further test of the validity of the freezing point method is supplied by a calculation of the activity of water from the freezing points and from vapor pressure. The latter data were obtained from the International Critical Tables,<sup>17</sup> and in the calculation of the activity coefficient it was assumed that the fugacity, f, equals the pressure, p; that is,

$$\frac{f}{f^0} = \frac{p}{p^0} = a_1''$$

TABLE VI  
Calculation of  $p/p^0$

| m   | $\frac{p^0-p}{mp^0}$ | $\frac{p^0-p}{p^0}$ | $p/p^0$ |
|-----|----------------------|---------------------|---------|
| 1.0 | .0330                | .0330               | .9670   |
| 2.0 | .0342                | .0684               | .9316   |
| 2.8 | .0353                | .0988               | .9012   |
| 4.0 | .0372                | .1484               | .7972   |

To calculate the activity of the water from the freezing point the following equation was used:

$$\log a_1'' = \frac{A, \bar{V}}{2.3026} + \frac{B, \bar{V}^2}{2 \cdot 2.3026} + \frac{C, \bar{V}^3}{3 \cdot 2.3026} + x$$

where the various quantities have the same meaning as in the

<sup>15</sup>Randall and Rossini, J. Am. Chem. Soc. 57, 323 (1929).

<sup>16</sup>Young, Chem. Rev. loc cit.

<sup>17</sup>International Critical Tables (New York: McGraw-Hill Book Company, Inc., 1928).



TABLE VII

Calculation of  $a_1''$  from freezing point data

| m   | $v$    | $\frac{A_1 v}{2.3026}$ | $\frac{B_1 v^2}{2(2.3026)}$ | $\frac{C_1 v^3}{3(2.3026)}$ | Log $a_1$ | $a_1$  | x      | $a_1''$ |
|-----|--------|------------------------|-----------------------------|-----------------------------|-----------|--------|--------|---------|
| 1.0 | 3.383  | -.014260               | -.000025                    | .000001                     | .985716-1 | .98764 | .99906 | .9667   |
| 2.0 | 6.965  | -.029317               | -.000104                    | .000012                     | .970591-1 | .93453 | .99645 | .9312   |
| 2.8 | 10.099 | -.042507               | -.000220                    | .000037                     | .957312-1 | .90638 | .99351 | .9005   |
| 4.0 | 15.376 | -.064719               | -.000509                    | .000131                     | .934916-1 | .86083 | .98820 | .8507   |

calculation of the activity coefficient of the solute.

A comparison of the results is shown in Table VIII.

TABLE VIII

| m   | $a_1^w$ (f.pt.) | $a_1^w$ (v.p.) | % diff. |
|-----|-----------------|----------------|---------|
| 1   | .9667           | .9670          | .03     |
| 2   | .9312           | .9316          | .04     |
| 2.8 | .9005           | .9012          | .08     |
| 4   | .8507           | .8512          | .06     |

The results of the two methods are in excellent agreement.

## SUMMARY

The ratio of the activity coefficient,  $\gamma$ , of sodium chloride in aqueous solution, to the value of  $\gamma$  of 0.1 molal sodium chloride has recently been determined by electromotive force methods. The same ratios, calculated from existing cryoscopic data, were not in good agreement with those obtained from electromotive force measurements. The cause of the discrepancy seemed to lie in the freezing point data.

Apparatus was designed for the investigation of the freezing points of concentrated solutions. A double thermostat was provided so that both the freezing mixture and the ice-water reference mixture could be surrounded by a bath at approximately their own respective freezing temperatures. Heat leaks, which affect the maintenance of a state of equilibrium necessary for an accurate freezing point determination, were reduced in this way.

The freezing points of aqueous sodium chloride solutions have been determined in the range from 0.1 to about 4.65 molal. A comparison of the value of the ratio,  $\gamma/\gamma_{0.1}$ , calculated from these freezing points and from electromotive force data shows excellent agreement.

A calculation of the activity of water in sodium chloride solutions from the freezing point data was compared with a similar calculation based on vapor pressure data. The two values for the activity of water in a 4.0 molal sodium chloride solution agreed within 0.06 per cent.

# APPENDIX I

## Explanation of the Symbols Used in the Text.

$\gamma$ , activity coefficient.

m, molality.

$\gamma_m$ , activity coefficient at m molal.

$L_1$ , relative heat content of the solvent.

$$j = 1 - \frac{\nu}{\nu \lambda m}.$$

$\nu$ , the freezing point lowering.

$\lambda$ , the molal freezing point lowering. For water this equals 1.858°C.

$\nu$ , the number of particles formed by the solute per molecule when in solution. For sodium chloride in aqueous solution,  $\nu$  equals 2.

$$A_1 = \frac{\Delta H_\theta}{R\theta^2} = -\frac{1}{55.508\lambda}.$$

$$\Delta H_\theta = -1436.7 \text{ cal. mole}^{-1}.$$

$$\theta = 273.18 \text{ K}^\circ.$$

$$R = 1.9864 \text{ cal. mole}^{-1} \text{ deg.}^{-1}.$$

$$B_1 = \frac{2\Delta H_\theta}{R\theta^3} - \frac{\Delta F_\theta}{R\theta^2}.$$

$$\Delta F_\theta = -9.049 \text{ cal. mole}^{-1} \text{ deg.}^{-1}.$$

$$B_2 = -\frac{55.508}{2.3026} B_1.$$

$$C_1 = \frac{3\Delta H_\theta}{R\theta^4} - \frac{2\Delta F_\theta}{R\theta^3} + \frac{\Delta G_\theta}{2R\theta^2}$$

$$\Delta G_\theta = 0.0566 \text{ cal. mole}^{-1} \text{ deg.}^{-2}.$$

$$C_2 = -\frac{55.508}{2.3026} C_1.$$

$$x \equiv \log \frac{a_1''}{a_1'} = -\bar{L}_1 (T'')^\nu + (\bar{C}_{p1} - \bar{C}_{p1}^\circ)z + \Delta G_1 \Omega.$$

$a_1''$  = activity of the solvent.

$a_1'$  = activity of the solute.

$T''$ , temperature for the calculation. In this case all

APPENDIX I (Cont.)

results were calculated with  $T''$  equal to  $298.18^\circ\text{K}$ .

$$y = \frac{T'' - T'}{2.3026 RT'' T'}$$

$T' = 273.18 - \Delta$ , or the freezing point of a solution of a given concentration.

$\bar{C}_{p1}$ , partial molal heat capacity.

$$z = T''y - \frac{1}{R} \log \frac{T''}{T'}$$

$$\Delta = 298.18 \left\{ z + \frac{t' - 25}{2} y \right\}$$

$$t' = - \Delta$$

$f$ , fugacity.

$f^\circ$ , fugacity of the standard state (pure solvent).

$p$ , vapor pressure.

$p^\circ$ , vapor pressure of the standard state (pure solvent).

$N_1$ , mole fraction of the solvent.

$N_2$ , mole fraction of the solute.

APPENDIX II

List of Special Apparatus Used In  
This Investigation

White Potentiometer, Leeds and Northrup Company, No.  
112177.

Type HS Galvanometer, used in connection with the White  
Potentiometer; Resistance 40 ohms; Leeds and Northrup Company,  
No. 196145.

Resistance Thermometer, Leeds and Northrup Company,  
No. 103770.

Mueller Wheatstone Bridge, Leeds and Northrup Company,  
No. 57347.

Type HS Galvanometer, used in connection with the Mueller  
Bridge; Resistance 19.2 ohms; Leeds and Northrup Company No. 179715.

For the special equipment used in the conductivity  
apparatus the reader is referred to the dissertation of N. J.  
Anderson, The University of Chicago, 1934.







